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Spectrophotometric determination of nickel by adsorption of its α-benzildioxime complex on naphthalene

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A method is described for the spectrophotometric determination of trace amounts of nickel after adsorption of its α-benzildioxime complex on naphthalene. α-benzildioxime forms a water-insoluble complex with nickel, which is quantitatively adsorbed on naphthalene. The mixture of the complex and naphthalene is dissolved in dimethylformamide and the trace amount of nickel is determined spectrophotometrically. Beer's law was obeyed for nickel concentration of 3-67 μg in 10 ml of dimethylformamide. The various factors such as pH, amounts of reagent and naphthalene, wavelength, digestion time, shaking time, standing time and diverse ions were studied. This complex was stable in both naphthalene and naphthalene-dimethylformamide solution.

1 Introduction

Spectrophotometric determination of metals after extraction of metal complexes with organic solvents such as chloroform or benzene as well as naphthalene has been used for the analysis of the trace amounts of metals. We have developed a new method involving spectrophotometric determination of metals by adsorption of metal complexes on naphthalene, and the method has been successfully applied to the analysis of trace amounts of metals[1]. In this communication, the determination of nickel is reported. Nickel reacts with α-benzildioxime to form a water-insoluble red colored complex. This complex is quantitatively adsorbed on microcrystalline naphthalene by vigorous shaking for a few seconds. The adsorbed mixture of the complex and naphthalene is separated from the aqueous solution by aspiration and dissolved in dimethylformamide. The absorbance of the solution is measured at 406 nm to determine trace amount of nickel. The adsorption of the complex on naphthalene is very rapidly attained by vigorous shaking for a few seconds. The

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amount of naphthalene for complete adsorption of the complex is very small, and the complex is almost completely adsorbed and concentrated from the larger volume of aqueous solution with only 0.6 g of naphthlene.

2 Experimental method

2.1 Reagents

Standard nickel solution(10 ppm) was prepared by diluting 10 ml of 1000 ppm standard nickel solution(Analytical-reagent grade, Wako Pure Chemical Co. Osaka, Japan) to 1000 ml with water.

α-benzildioxime acetone solution(0.04%) was prepared by dissolving 0.04 g of α-benzildioxime in 100 ml of acetone.

Naphthalene-acetone solution(20%) was prepared by dissolving 20 g of naphthalene in 100 ml of acetone.

The buffer solutions were prepared by mixing suitable amounts of 1M acetic acid and 1M ammonium acetate solution for pH 3-6, or 1M ammonia water and 1M ammonium acetate solution for pH 8-11.

All other chemicals were of analytical-reagent grade and were not purified further.

Deionized water was used.

2.2 Apparatus

A Hitachi Model 200-20 double beam spectrophotometer was used for the absorbance measurements with 10 mm glass cell and the pH measurements were made a Toa-Dempa HM-6A pH meter, equipped with combined glass and calomel electrodes.

2.3 Procedure

To about 40 ml of a series of sample solution containing 1-6 ml of 10 ppm standard nickel solution, in a tightly stoppered Erlenmeyer flask, add 5.0 ml of 0.04% α-benzildioxime acetone solution and 2.0 ml of the buffer solution(pH 9.5). Mix the solution well, and let stand it to digest for 5 min. Add 2.0 ml of 20% naphthalene-acetone solution and shake it vigorously for 1 min. Collect the mixture of the complex and naphthalene on a funnel with disc shaped filter(No. 5C filter paper, Toyo Roshi Co. Osaka, Japan) or glass filter(No. 2 or 3). Wash with water and dry in a dryer if necessary. Then dissolve it in dimethylformamide and dilute to 10 ml. Measure the absorbance of the solution in 10 mm glass cell against a reagent blank prepared similarly. Calculate the amount of nickel from a calibration curve.

3 Results and discussion

3.1 Absorption spectra

Sample solution containing 40 μg of nickel, 2.0 ml of the buffer solution(pH 9.5) and 5.0 ml of 0.04% α-benzildioxime acetone solution was prepared according to the recommended procedure, and the complex formed was adsorbed on microcrystalline naphthalene by vigorous shaking for 1 min. The adsorbed mixture of the complex and naphthalene was dissolved in dimethylformamide, and the absorbance of the solution was measured at the wavelengths between 320 and 500 nm against water. Figure 1 shows the absorption spectra of the nickel complex and the reagent blank in naphthalene-dimethylformamide solution. The curve of the complex has two peaks at 360 and 406 nm. At these wavelengths, the absorbance due to the reagent blank was negligible in the comparison with that of the complex. Therefore, 406 nm was chosen as the most suitable wavelength.

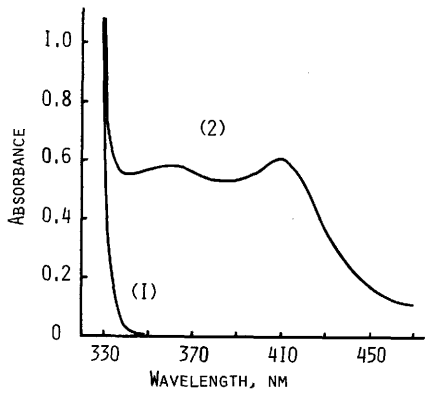

FIG. 1 ABSORPTION SPECTRA OF α-BENZILDIOXIME AND NICKEL COMPLEX IN NAPHTHALENE-DMF SOLUTION
NI : 40 μG ; 0.04% α-BENZILDIOXIME : 5.0 ML ; PH : 9.5 ; 20% NAPHTHALENE-ACETONE : 2.0 ML
REFERENCE : WATER ; (I) REAGENT BLANK ; (2) NICKEL COMPLEX

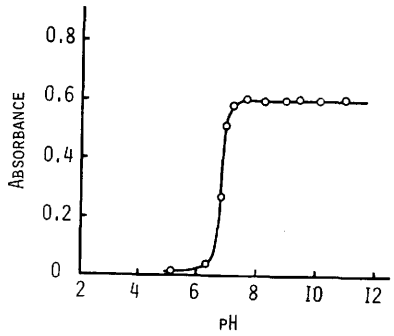

FIG. 2 EFFECT OF PH
NI : 40 μG ; 0.04% α-BENZILDIOXIME : 5.0 ML ; WAVELENGTH : 406 NM ; 20% NAPHTHALENE-ACETONE : 2.0 ML ; SHAKING TIME : I MIN
REFERENCE : REAGENT BLANK

3.2 Effect of pH

The relationship between the absorbance and the pH of the solution after adsorption was investigated in the pH range 5.0-11.0. The result obtained is shown in Fig.2. From this experiment, the adsorption starts from pH 6.3, increases sharply with increasing pH and reaches the maximum and constant over the pH range 7.5-11.0. Therefore, the pH of the solution was adjusted to 9.5 for further work.

3.3 Effect of reagent concentartion

Various amounts of α-benzildioxime were added to the solution containing 40 μg of nickel and 2.0 ml of the buffer solution(pH 9.5), and the effect of variation in the α-benzildioxime concentration on the absorbance of the comylex has been studied. The result obtained is shown in Fig.3. It indicates that 1.0-7.0 ml of 0.04% solution are quite appropriate for the quantitative adsorption of nickel.

3.4 Effect of buffer solution and naphthalene concentration

Varying amounts of the buffer solution(pH 9.5) were added to the solution containing 40 μg of nickel and 5.0 ml of 0.04% α-benzildioxime acetone solution, and the adsorption of the complex was carried out according to the recommended procedure. From the experimental result, volumes of buffer solution of 0.5-5.0 ml gave essentially the same absorbance.

The various volume of 20% naphthalene-acetone solution was added to the solution containing the nickel complex. Figure 4 shows the effect of addition of naphthalene solution on the absorbance. From this experiment, the addition of 0.3-7.0 ml of 20% naphthalene solution did not cause any variation in the absorbance.

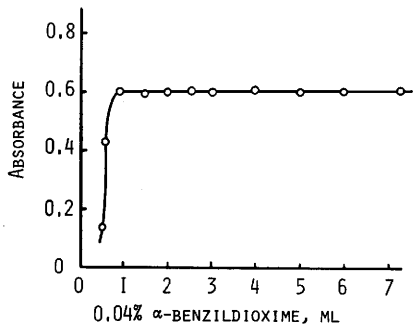

FIG. 3 EFFECT OF REAGENT CONCENTRATION
Ni : 40 μg ; WAVELENGTH : 406 nm ; pH : 9.5 ; SHAKING TIME : 1 min
REFERENCE : REAGENT BLANK

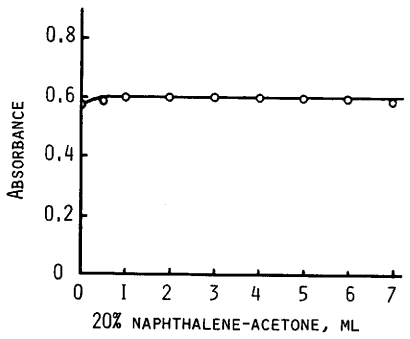

FIG. 4 EFFECT OF NAPHTHALENE CONCENTRATION
Ni : 40 μg ; pH : 9.5 ; WAVELENGTH : 406 nm ; 0.04% α-BENZILDIOXIME : 5.0 ml ; SHAKING TIME : 1 min ; STANDING TIME : 10 min
REFERENCE : REAGENT BLANK

3.5 Effect of volume of aqueous phase

The effect of volume of the aqueous phase on the absorbance was investigated to the recommended procedure. Table 1 shows that 50-1000 ml of the aqueous phase have almost no effect on the absorbance of the complex.

3.6 Effect of shaking time and standing time

Table 1 Effect of volume ofaqueous phase

Volume of aqueous phase (ml)	Absorbance	Volume of aqueous phase (ml)	Absorbance
50	0.600	1000	0.585
100	0.620	1200	0.510
300	0.590	1400	0.550
400	0.582	1600	0.458
500	0.613	1800	0.482
800	0.615	2000	0.415
900	0.600		

Ni : 40 μg ; pH : 9.5 ; Digestion time(40-50°C) : 30 min ;

Two ml of 20% naphthalene acetone solution were added to the sample solution containing the complex, and the adsorption of the complex on naphthalene was carried out by vigorous shaking for 3-180 sec. This period of shaking time was demonstraetd to be quite sufficient for the complete adsorption of the complex.

The color of the complex in naphthalene-dimethylformamide solution was stable for some hours and gave no change in the absorbance.

3.7 Choice of solvent

The tests were made with various organic solvents to dissolve the mixture of the nickel complex and naphthalene. The complex is soluble in dimethylformamide, chloroform, DMSO and dioxane, but insoluble in benzene, toluene, xylene, chlorobenzene, ethylene dichloride, isoamyl-acetate, propylene carbonate, etc. even at 50-60 °C.

3.8 Calibration curve

Under the optimum conditions described above, the calibration curve for the nickel determination was constructed. Beer's law was obeyed over the range 3-67 μg of nickel in 10 ml of dimethylformamide. The molar absorptivity was calculated to be 9.0×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$, the sensitivity being 0.0066 μg of nickel per cm^2 for the absorbance of 0.001. The precision of this method was estimated with 10 samples containing 40 μg of nickel. A mean absorbance at 406 nm was 0.600 with a standard deviation of 6.7×10^{-3}, or a relative standard deviation of 1.10%.

3.9 Effect of diverse ions

The effect of the diverse ions was examined with the solution containing 40 μg of nickel and various amounts of diverse ions(alkali metal salts or metal ions). The pH of the solution was adjusted to about 9.5.

The results obtained are shown in Tables 2 and 3. The following alkali metal salts and metal ions did not interfere : Na_2SO_4, NaCl, NH_4Cl, KNO_3, $NaH_2PO_4 \cdot 2H_2O$, CH_3COONa, $Na_2HPO_4 \cdot 12H_2O$, sodium tartrate, sodium citrate, sodium oxalate, Na_2SO_3, Hg^{2+}, Cr^{6+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}. Na_2CO_3, KBr, KCN, EDTA gave negative interference and Fe^{3+}, Cu^{2+}, Co^{2+}, Bi^{3+} did positive one. Especially small amounts of KCN and EDTA interfered seriously.

Table 2 Effect of diverse alkali metal salts

Alkali metal salts	Amounts added(mg)	Absorbance
—	—	0.600
Na_2SO_4	100	0.600
"	500	0.601
NaCl	100	0.603
"	500	0.602
NH_4Cl	100	0.595
"	500	0.607
$NaH_2PO_4 \cdot 2H_2O$	100	0.602
"	500	0.607
Na_2CO_3	20	0.600
"	50	0.587
"	100	0.580
"	500	0.566
KNO_3	100	0.597
"	500	0.599
KBr	50	0.608
"	100	0.590
"	500	0.575
CH_3COONa	100	0.588
"	500	0.592
$Na_2HPO_4 \cdot 12H_2O$	200	0.596
"	500	0.601

Sodium tartrate	100	0.592
"	500	0.610
Sodium citrate	100	0.597
"	500	0.599
Sodium oxalate	100	0.603
"	500	0.599
Na_2SO_3	100	0.605
"	500	0.600
KCN	0.02	0.597
"	0.03	0.594
"	0.06	0.565
"	0.20	0.354
Disodium EDTA	0.01	0.600
"	0.03	0.535
"	0.10	0.351
"	0.20	0.153

Ni : 40 μg ; pH : 9.5 ; Digestion time : 10 min

Table 3 Effect of diverse metal ions

Metal ions	Amounts added(μg)	Absorbance
—	—	0.600
Fe^{3+}	20	0.596
"	50	0.607
"	100	0.641
Cu^{2+}	10	0.621
"	20	0.648
"	50	0.761
"	100	0.940
Co^{2+}	5	0.603
"	10	0.608
"	20	0.618

"	50	0.692
"	100	0.736
Bi^{3+}	50	0.610
"	100	0.647
"	200	0.700
Hg^{2+}	100	0.604
"	200	0.600
Cr^{6+}	100	0.611
"	200	0.613
Pb^{2+}	100	0.606
"	200	0.615
Zn^{2+}	100	0.602
"	200	0.612
Cd^{2+}	100	0.606
"	200	0.603
Ca^{2+}	1000	0.604
"	2000	0.603
Mg^{2+}	1000	0.594
"	2000	0.593
Mn^{2+}	100	0.598
"	200	0.595

Ni : 40 µg ; pH : 9.5 ; Digestion time : 10 min ;

Reference

1) M.Satake, Y. Matsumura, T. Fujinaga and Y. Takagi : Bunseki Kagaku, 1978, 27, 486.